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## Structure Reports

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## 5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

Daniel Teoh-Chuan Tan,<sup>a</sup> Hasnah Osman,<sup>a‡</sup> Azlina Harun Kamaruddin,<sup>b</sup> Samuel Robinson Jebas<sup>c§</sup> and Hoong-Kun Fun<sup>c\*</sup><sup>a</sup>School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, <sup>b</sup>School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia, and <sup>c</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia  
Correspondence e-mail: hkfun@usm.my

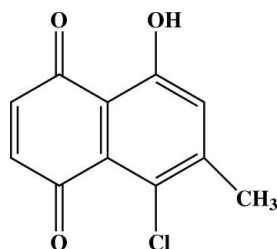
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.109; data-to-parameter ratio = 29.3.

The molecule of the title compound,  $\text{C}_{11}\text{H}_7\text{ClO}_3$ , is planar, with a maximum deviation of 0.0383 (10) Å from the naphthoquinone plane. An intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond generates an  $S(6)$  ring motif. The crystal packing is stabilized by intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. Short intramolecular  $\text{Cl}\cdots\text{O}$  [2.8234 (8) Å] and  $\text{O}\cdots\text{O}$  [2.5530 (11) Å], and intermolecular  $\text{Cl}\cdots\text{Cl}$  [3.2777 (3) Å] contacts further stabilize the crystal structure.

## Related literature

For the biological activity of the related compound 7-methyljuglone, see: Mahapatra *et al.* (2007); Van der Kooy & Meyer (2006). For the synthesis of 7-methyljuglone from the title compound, see: Musgrave & Skoyles (2001); Mahapatra *et al.* (2007). For bond-length data, see: Allen *et al.* (1987). For graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).

<sup>‡</sup> Additional Correspondence author e-mail: ohasnah@usm.my.<sup>§</sup> Permanent address: Department of Physics, Karunya University, Karunya Nagar, Coimbatore 641114, India.

## Experimental

## Crystal data

 $\text{C}_{11}\text{H}_7\text{ClO}_3$   
 $M_r = 222.62$   
Monoclinic,  $C2/c$   
 $a = 10.7546$  (1) Å  
 $b = 10.3104$  (1) Å  
 $c = 16.8370$  (2) Å  
 $\beta = 100.285$  (1)°  
 $V = 1836.96$  (3) Å<sup>3</sup>  
 $Z = 8$   
Mo  $K\alpha$  radiation  
 $\mu = 0.40$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.30 \times 0.21 \times 0.14$  mm

## Data collection

Bruker SMART APEXII CCD  
area-detector diffractometer  
Absorption correction: multi-scan  
(SADABS; Bruker, 2005)  
 $T_{\min} = 0.891$ ,  $T_{\max} = 0.945$   
17328 measured reflections  
4015 independent reflections  
3356 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.109$   
 $S = 1.07$   
4015 reflections  
137 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.61$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H1O3}\cdots\text{O2}$	0.86	1.73	2.5530 (11)	161
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{i}}$	0.93	2.51	3.4124 (12)	163
$\text{C3}-\text{H3A}\cdots\text{O2}^{\text{ii}}$	0.93	2.57	3.3000 (12)	136

Symmetry codes: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $-x + 1, y, -z + \frac{1}{2}$ .

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2597).

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**supplementary materials**

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## 5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

D. T.-C. Tan, H. Osman, A. H. Kamaruddin, S. R. Jebas and H.-K. Fun

### Comment

5-Hydroxy-7-methyl-1,4-naphthoquinone (7-methyljuglone) has recently been reported to exhibit activity against *Mycobacterium tuberculosis* (Van der Kooy & Meyer, 2006; Mahapatra *et al.*, 2007). Naturally occurring 7-methyljuglone is synthesised from 8-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone in high yield (Musgrave & Skoyles, 2001; Mahapatra *et al.*, 2007). This paper reports the molecular structure of 8-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone; the precursor to synthetic 7-methyljuglone.

The asymmetric unit of (I) consists of one molecule of 8-Chloro-5-hydroxy-7-methyl-1,4-naphthoquinone. The naphthoquinone ring is essentially planar with the maximum deviation from planarity being 0.0383 (10) Å for atom C8. The bond lengths in (I) have normal values (Allen *et al.*, 1987).

An intramolecular O–H...O hydrogen bond generates an S(6) ring motif (Bernstein *et al.*, 1995). The crystal packing is stabilized by intermolecular C–H...O hydrogen bonds (Table 2) (Fig 2). Short intramolecular Cl...O = 2.8234 (8) Å; O...O = 2.5530 (11) Å and intermolecular Cl...Cl<sup>i</sup> = 3.2777 (3) Å [symmetry code: (i) 1 - x, y, 3/2 - z] contacts further stabilize the crystal packing.

### Experimental

The title compound was prepared from the Friedel-Crafts acylation of 4-chloro-3-methylphenol with maleic anhydride (Musgrave & Skoyles, 2001). Repeated Soxhlet extraction of the crude Friedel-Crafts product with n-hexane, and silica gel column chromatography purification [chloroform and n-hexane (1:9)] of the n-hexane extract afforded the title compound. Finally, slow evaporation of a n-hexane solution at 305 K gave single crystals of the title compound.

### Refinement

H atoms were positioned geometrically [C–H = 0.93 (aromatic) or 0.96 Å (methyl)] and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$  and  $1.5U_{\text{eq}}(\text{methyl C})$ . A rotating-group model was used for the methyl groups. The O bound hydrogen atom was located from the Fourier map and refined isotropically with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .

### Figures

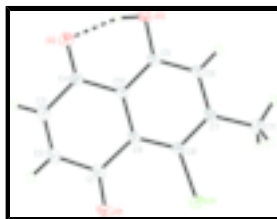


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. The intramolecular H bond is drawn as a dashed line.

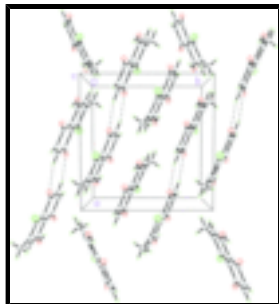


Fig. 2. The crystal packing of the title compound, viewed along the *c* axis, showing dimer formation. Dashed lines indicate the hydrogen bonding.

### 5-Chloro-8-hydroxy-6-methyl-1,4-naphthoquinone

#### Crystal data

$C_{11}H_7ClO_3$

$M_r = 222.62$

Monoclinic,  $C2/c$

Hall symbol:  $-C 2yc$

$a = 10.7546$  (1) Å

$b = 10.3104$  (1) Å

$c = 16.8370$  (2) Å

$\beta = 100.285$  (1)°

$V = 1836.96$  (3) Å<sup>3</sup>

$Z = 8$

$F_{000} = 912$

$D_x = 1.610$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 6307 reflections

$\theta = 2.8$ – $30.1$ °

$\mu = 0.40$  mm<sup>-1</sup>

$T = 100$  K

Block, red

$0.30 \times 0.21 \times 0.14$  mm

#### Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$  K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.891$ ,  $T_{\max} = 0.945$

17328 measured reflections

4015 independent reflections

3356 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 35.1$ °

$\theta_{\text{min}} = 2.8$ °

$h = -12 \rightarrow 17$

$k = -16 \rightarrow 16$

$l = -27 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.109$

$S = 1.07$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.6106P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

4015 reflections  $\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$   
 137 parameters  $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$   
 Primary atom site location: structure-invariant direct methods Extinction correction: none

*Special details*

**Experimental.** The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.60008 (2)	0.08776 (3)	0.687132 (14)	0.02314 (8)
O1	0.40351 (7)	0.18970 (8)	0.57005 (5)	0.02395 (16)
O2	0.64859 (7)	0.18264 (8)	0.31989 (4)	0.02085 (15)
O3	0.83772 (7)	0.06289 (8)	0.40048 (4)	0.02028 (14)
H1O3	0.7847	0.1042	0.3653	0.030*
C1	0.46492 (8)	0.18621 (9)	0.51561 (6)	0.01565 (16)
C2	0.40771 (9)	0.23850 (9)	0.43571 (6)	0.01789 (17)
H2A	0.3271	0.2743	0.4292	0.021*
C3	0.46720 (9)	0.23648 (9)	0.37229 (6)	0.01852 (17)
H3A	0.4275	0.2710	0.3232	0.022*
C4	0.59410 (9)	0.18056 (9)	0.37912 (5)	0.01556 (16)
C5	0.77541 (8)	0.06817 (8)	0.46273 (6)	0.01477 (15)
C6	0.83488 (8)	0.01527 (9)	0.53621 (6)	0.01568 (16)
H6A	0.9135	-0.0238	0.5394	0.019*
C7	0.77959 (8)	0.01969 (9)	0.60416 (5)	0.01563 (15)
C8	0.65972 (8)	0.07923 (9)	0.59849 (5)	0.01508 (15)
C9	0.59512 (8)	0.12905 (8)	0.52543 (5)	0.01356 (15)
C10	0.65466 (8)	0.12451 (8)	0.45647 (5)	0.01354 (15)
C11	0.84754 (10)	-0.03753 (11)	0.68182 (6)	0.02193 (19)
H11A	0.9265	-0.0738	0.6736	0.033*
H11B	0.7964	-0.1044	0.6993	0.033*
H11C	0.8632	0.0290	0.7222	0.033*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

$U^{11}$   $U^{22}$   $U^{33}$   $U^{12}$   $U^{13}$   $U^{23}$

## supplementary materials

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C11	0.02101 (12)	0.03306 (14)	0.01720 (11)	0.00279 (9)	0.00841 (8)	0.00089 (8)
O1	0.0164 (3)	0.0311 (4)	0.0264 (4)	0.0055 (3)	0.0096 (3)	-0.0001 (3)
O2	0.0206 (3)	0.0258 (3)	0.0170 (3)	0.0004 (3)	0.0055 (3)	0.0009 (3)
O3	0.0172 (3)	0.0258 (3)	0.0200 (3)	0.0053 (3)	0.0093 (3)	0.0014 (3)
C1	0.0117 (3)	0.0146 (3)	0.0210 (4)	0.0004 (3)	0.0040 (3)	-0.0023 (3)
C2	0.0123 (4)	0.0162 (4)	0.0243 (4)	0.0018 (3)	0.0009 (3)	-0.0017 (3)
C3	0.0150 (4)	0.0188 (4)	0.0206 (4)	0.0015 (3)	0.0000 (3)	0.0006 (3)
C4	0.0146 (4)	0.0150 (3)	0.0170 (4)	-0.0012 (3)	0.0027 (3)	-0.0009 (3)
C5	0.0122 (3)	0.0152 (3)	0.0181 (4)	-0.0003 (3)	0.0058 (3)	-0.0017 (3)
C6	0.0115 (3)	0.0164 (4)	0.0193 (4)	0.0008 (3)	0.0034 (3)	-0.0012 (3)
C7	0.0126 (3)	0.0168 (4)	0.0171 (4)	-0.0006 (3)	0.0017 (3)	-0.0010 (3)
C8	0.0130 (3)	0.0174 (4)	0.0154 (4)	-0.0011 (3)	0.0043 (3)	-0.0013 (3)
C9	0.0103 (3)	0.0137 (3)	0.0172 (4)	-0.0002 (3)	0.0040 (3)	-0.0017 (3)
C10	0.0113 (3)	0.0141 (3)	0.0156 (3)	0.0001 (3)	0.0033 (3)	-0.0014 (3)
C11	0.0189 (4)	0.0279 (5)	0.0177 (4)	0.0024 (4)	-0.0001 (3)	0.0016 (3)

### *Geometric parameters (Å, °)*

C11—C8	1.7287 (9)	C5—C6	1.3980 (13)
O1—C1	1.2222 (12)	C5—C10	1.4092 (12)
O2—C4	1.2438 (11)	C6—C7	1.3812 (13)
O3—C5	1.3423 (11)	C6—H6A	0.9300
O3—H1O3	0.8581	C7—C8	1.4156 (13)
C1—C2	1.4777 (14)	C7—C11	1.5002 (13)
C1—C9	1.5008 (12)	C8—C9	1.3980 (13)
C2—C3	1.3393 (14)	C9—C10	1.4234 (12)
C2—H2A	0.9300	C11—H11A	0.9600
C3—C4	1.4670 (13)	C11—H11B	0.9600
C3—H3A	0.9300	C11—H11C	0.9600
C4—C10	1.4667 (13)		
C5—O3—H1O3	99.0	C6—C7—C8	118.69 (8)
O1—C1—C2	118.62 (8)	C6—C7—C11	119.62 (8)
O1—C1—C9	123.19 (9)	C8—C7—C11	121.69 (8)
C2—C1—C9	118.18 (8)	C9—C8—C7	121.48 (8)
C3—C2—C1	122.65 (8)	C9—C8—C11	122.56 (7)
C3—C2—H2A	118.7	C7—C8—C11	115.95 (7)
C1—C2—H2A	118.7	C8—C9—C10	118.71 (8)
C2—C3—C4	120.92 (9)	C8—C9—C1	123.27 (8)
C2—C3—H3A	119.5	C10—C9—C1	118.02 (8)
C4—C3—H3A	119.5	C5—C10—C9	119.69 (8)
O2—C4—C10	121.37 (8)	C5—C10—C4	119.08 (8)
O2—C4—C3	119.69 (8)	C9—C10—C4	121.21 (8)
C10—C4—C3	118.94 (8)	C7—C11—H11A	109.5
O3—C5—C6	117.51 (8)	C7—C11—H11B	109.5
O3—C5—C10	122.69 (8)	H11A—C11—H11B	109.5
C6—C5—C10	119.80 (8)	C7—C11—H11C	109.5
C7—C6—C5	121.57 (8)	H11A—C11—H11C	109.5
C7—C6—H6A	119.2	H11B—C11—H11C	109.5
C5—C6—H6A	119.2		

O1—C1—C2—C3	-178.75 (9)	O1—C1—C9—C8	-2.55 (14)
C9—C1—C2—C3	0.15 (13)	C2—C1—C9—C8	178.61 (8)
C1—C2—C3—C4	0.34 (14)	O1—C1—C9—C10	176.82 (9)
C2—C3—C4—O2	-178.28 (9)	C2—C1—C9—C10	-2.03 (12)
C2—C3—C4—C10	1.01 (14)	O3—C5—C10—C9	-178.76 (8)
O3—C5—C6—C7	178.08 (8)	C6—C5—C10—C9	1.06 (13)
C10—C5—C6—C7	-1.75 (13)	O3—C5—C10—C4	-0.34 (13)
C5—C6—C7—C8	0.12 (13)	C6—C5—C10—C4	179.48 (8)
C5—C6—C7—C11	-179.54 (9)	C8—C9—C10—C5	1.20 (13)
C6—C7—C8—C9	2.23 (13)	C1—C9—C10—C5	-178.19 (8)
C11—C7—C8—C9	-178.11 (9)	C8—C9—C10—C4	-177.18 (8)
C6—C7—C8—C11	-177.07 (7)	C1—C9—C10—C4	3.43 (12)
C11—C7—C8—C11	2.59 (12)	O2—C4—C10—C5	-2.09 (13)
C7—C8—C9—C10	-2.87 (13)	C3—C4—C10—C5	178.63 (8)
C11—C8—C9—C10	176.38 (7)	O2—C4—C10—C9	176.30 (8)
C7—C8—C9—C1	176.48 (8)	C3—C4—C10—C9	-2.98 (13)
C11—C8—C9—C1	-4.26 (12)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1O3 $\cdots$ O2	0.86	1.73	2.5530 (11)	161
C2—H2A $\cdots$ O1 <sup>i</sup>	0.93	2.51	3.4124 (12)	163
C3—H3A $\cdots$ O2 <sup>ii</sup>	0.93	2.57	3.3000 (12)	136

Symmetry codes: (i)  $-x+1/2, -y+1/2, -z+1$ ; (ii)  $-x+1, y, -z+1/2$ .



Fig. 1

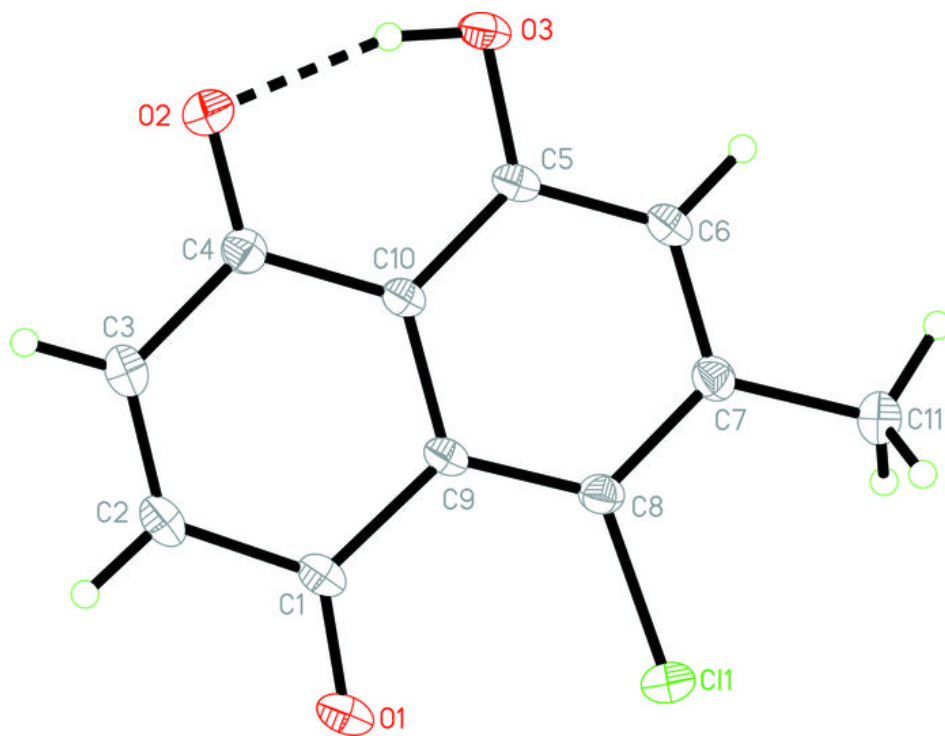


Fig. 2

